Journal of Alloys and Compounds 503 (2010) L5–L8

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Letter

TEM and ED confirmation of conversion of 3D and 2D perovskite-type into fluorite-type structure

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ARTICLE INFO

Article history:
Received 19 February 2010
Received in revised form 30 April 2010
Accepted 30 April 2010
Available online 7 May 2010

Keywords:
CO_2 capture synthesis
Solid–gas phase synthesis
$Ce_{1-x}M_xO_{2-\delta}$ (M = In
Y)
Electron diffraction
High-resolution transmission electron microscopy
Metastable fluorites

ABSTRACT

In this paper, we confirm the transformation of three-dimensional (3D) In-doped perovskite-like $BaCe_{1-x}In_xO_{3-\delta}$ ($x = 0.1$; 0.2) and layered (two-dimensional) perovskite-related $Sr_2Ce_{1-x}Y_xO_{4-\delta}$ ($x = 0.1$; 0.2) into corresponding fluorite-type $Ce_{1-x}M_xO_{2-\delta}$ (M = In, Y) under CO_2 mediated reaction at elevated temperature, respectively, using high-resolution transmission electron microscopy (HRTEM) and electron diffraction (ED) studies. HRTEM images confirmed expected nano-sized materials and ED study showed the formation of a single-phase fluorite-type CeO_2 structure and absence of ED patterns resulting from the perovskite-like precursors and potential reaction by-products such as In_2O_3 and Y_2O_3 after the CO_2 reaction, which is consistent with ex situ and in situ powder X-ray diffraction (PXRD), and strongly support the proposed structural transformation reactions.

1. Introduction

Design and preparation of solid-state functional property materials for specific applications, including fuel cells, batteries, sensors, thermoelectrics, photovoltaics, dielectrics, electronics, and catalysts, have been routine work for several material chemists and scientists [1–6]. Solid-state materials are being commonly synthesized using a conventional mixed-oxide route, well known as a ceramic method, at elevated temperatures. Several low-temperature methods, also popularly called as *chimie-douce* synthesis, involve preparation of precursor materials by ceramic method and subsequently transformed into desired and designed novel metastable functional materials [3–9]. A well-known example is the synthesis of new modification of TiO_2 by a mild-dehydration of $H_2Ti_4O_9 \cdot H_2O$. The precursor $H_2Ti_4O_9 \cdot H_2O$ was prepared from the K-analogue $K_2Ti_4O_9$ (synthesized by ceramic reaction) by ion-exchange reaction [7]. Other significant examples are ion-exchange and double ion-exchange (metathesis reaction) of a large family of layered (2D) perovskite-like Dion-Jacobson (DJ) and Ruddlesden-Popper (RP)-type structures and inter-conversion of RP phase into Aurivillius structure and *vice-versa* [8–11]. Numerous metastable allotropes compounds were also prepared by gentle dehydration of proton and/or hydrated metal oxides in air or vacuum. Another synthesis method utilizes H_2 or inert atmospheres to prepare compounds containing lower valence cations than that of prepared in ambient condition.

Our group has employed a new two steps synthesis to stabilize indium-doped CeO_2 structure, which was not attainable by a regular mixed-oxide solid-state reaction at 800–1500 °C [12–15]. This approach involves leaching of alkaline from the perovskite and its related structure precursors under CO_2 at elevated temperatures and subsequent acid washing. In the literature, the chemical stability of doped perovskite-type ABO_3 (A = Sr, Ba, B = Ce, Zr) under CO_2 at elevated temperatures was well documented [16–24]. For example, Y_2O_3-doped $BaCeO_3$ (BCY) was found to be chemically unstable in pure CO_2 at elevated temperature according to the reaction $BaCe_{1-x}Y_xO_{2-\delta}(s) + CO_2(g) \xrightarrow{\Delta} BaCO_3(s) + Ce_{1-x}Y_xO_{3-\delta}(s)$ and partial substitution of Ti and or Zr for Ce in BCY improved the chemical stability in CO_2 [12,13,17,25–30]. Recently, Xie and others have investigated the effect of Sn, Ta and Nb substitution for Ce in BCY on chemical stability and proton conductivity [25–30].

It is very important to note that acceptor-doped ceria based materials are being considered as the potential electrolyte materials for the intermediate temperature solid oxide fuel cells (IT-SOFCs). Particularly, $Ce_{1-x}M_xO_{2-\delta}$ (M = Y, Sm, Gd) have drawn much attention because of their high oxide ion conductiv-

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0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2010.04.239

ity compared to Y_2O_3-doped ZrO_2 and SrO- and MgO-doped perovskite-like $LaGaO_3$ (LSGM) [31]. Furthermore, the doped CeO_2-based electrolytes appear to be chemically stable against reaction with Ni anode as well as several perovskite-type structure cathode materials such as $La_{1-x}Sr_xMO_3$ (M = Mn, Fe, Co) [32]. Accordingly, understanding of structure and morphology (particle size) of the fluorite-type $Ce_{1-x}M_xO_{2-\delta}$ (M = In, Y) compounds prepared from perovskites under CO_2 atmosphere is very useful for further development of ceria electrolytes. Also, the present work provides answer to a key question about phase purity of the fluorite-type product obtained after CO_2 reaction using electron diffraction (ED). In this letter, we confirm the formation a single-phase fluorite-type solid solution $Ce_{1-x}M_xO_{2-\delta}$ using high-resolution transmission electron microscopy (HRTEM) combined with ED and PXRD.

2. Experimental details

$Ce_{1-x}M_xO_{2-\delta}$ (M = In, Y; x = 0.1; 0.2) was synthesized by CO_2 mediated process from the perovskite-type $BaCe_{1-x}In_xO_{3-\delta}$ and layered $Sr_2Ce_{1-x}Y_xO_{4-\delta}$, respectively, at elevated temperature of 800 °C and subsequent acid washing using dilute mineral acids [11–13]. The precursors $BaCe_{1-x}In_xO_{3-\delta}$ and $Sr_2Ce_{1-x}Y_xO_{4-\delta}$ were prepared by a conventional ceramic method in air with final sintering temperature at 1500 °C and 1350 °C, respectively for 24 h, using appropriate amounts of high purity $SrCO_3$ (99+%, VWR International), $BaCO_3$ (99+%, VWR International), CeO_2 (99.5%, Alfa Aesar), and In_2O_3 (99.9%, Alfa Aesar). As-prepared samples after CO_2 reaction and subsequent acid washed were characterized using a powder X-ray diffraction (PXRD) (Bruker D8 powder X-ray diffractometer; CuKα, 40 kV, 40 mA) at room temperature.

Further characterization involves use of transmission electron microscopy (TEM) coupled with electron diffraction (ED). It was done on a FEI Tecnai F20 FEG-TEM (FEI, Eindhoven, The Netherlands) equipped with a Gatan Imaging Filter and a Gatan 860 GIF 2001 CCD of 1024 × 1024 resolution. Standard TEM was done at magnifications between 8000 and 67,000. HRTEM was performed at magnifications between 940,000 and 1,350,000. The diffraction patterns were taken at a camera length of 400 mm and directly after taking each individual diffraction pattern of the sample, it was exchanged by a reference sample of amorphous gold without changing any settings on the microscope. The diffraction rings of this amorphous gold were used to confirm a proper calibration in diffraction mode of the equipment.

3. Results and discussion

PXRD (Fig. 1) confirmed the formation of fluorite-type structure for $Ce_{1-x}M_xO_{2-\delta}$ (M = In, Y; x = 0.1; 0.2) from the corresponding $BaCe_{1-x}M_xO_{3-\delta}$ under CO_2 at elevated temperatures, which was

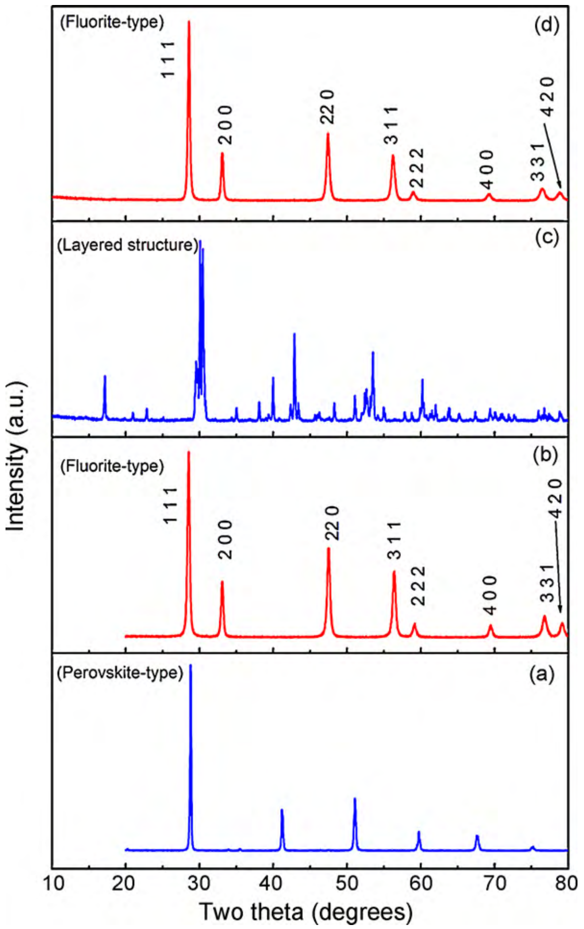

Fig. 1. PXRD patterns of (a) as-prepared perovskite-like structure $BaCe_{0.9}In_{0.1}O_{2.95}$, (b) after heating the sample "a" at 800 °C in CO_2 for 12 h and subsequently treated it with dilute acid and dried in ambient air, (c) K_2NiF_4-related layered perovskite-type structure of as-prepared $Sr_2Ce_{0.9}Y_{0.1}O_{3.95}$, (d) after heating the sample "c" at 800 °C in CO_2 for 12 h and subsequently treated it with dilute acid and dried in ambient air.

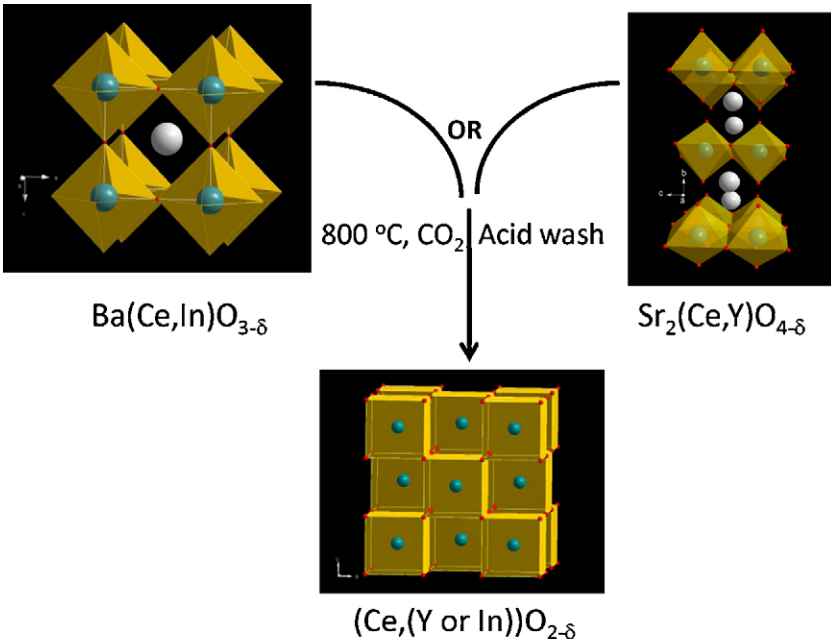

Fig. 2. Idealized crystal structure showing the formation of In and or Y-doped CeO_2 from the perovskite-like structure doped $BaCeO_3$ and perovskite-related layered structure doped Sr_2CeO_4 in CO_2 at elevated temperature and subsequent acid washing [14,15].

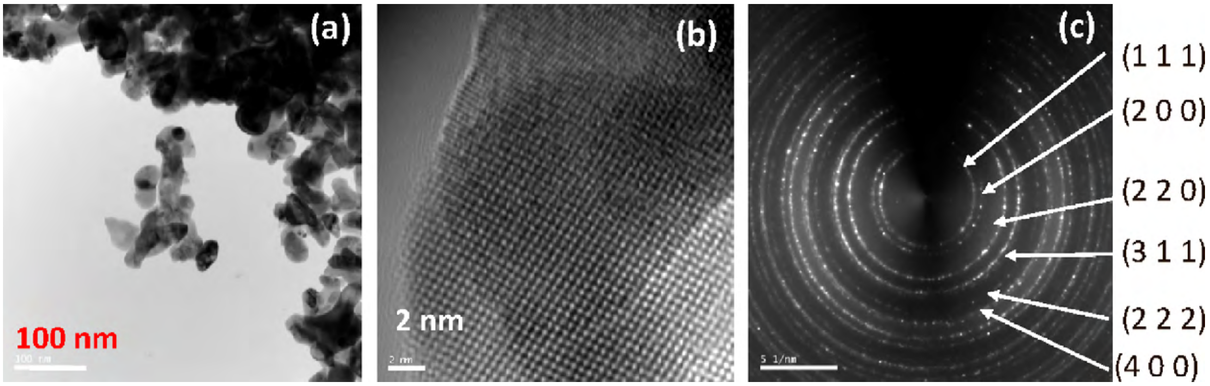

Fig. 3. TEM and HRTEM images of as-prepared (CO_2 capture method) powdered $Ce_{0.9}In_{0.1}O_{1.95}$ from the corresponding 10 mol% In-doped $BaCeO_3$: (a) 100 nm scale, (b) 2 nm scale and (c) selected area electron diffraction pattern.

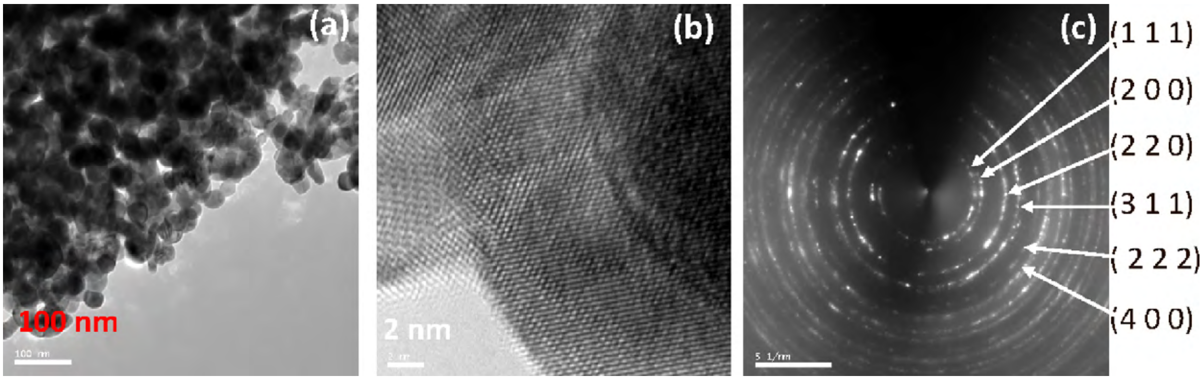

Fig. 4. TEM and HRTEM images of as-prepared (CO_2 capture method) powdered $Ce_{0.8}In_{0.2}O_{1.9}$ from the corresponding 20 mol% In-doped $BaCeO_3$: (a) 100 nm scale, (b) 2 nm scale and (c) selected area electron diffraction pattern.

found to be consistent with ex situ and in situ X-ray studies [12,14,15]. The PXRD of CO_2 mediated synthesized $Ce_{0.9}In_{0.1}O_{1.95}$, $Ce_{0.8}In_{0.2}O_{1.9}$, $Ce_{0.9}Y_{0.1}O_{1.95}$ and $Ce_{0.8}Y_{0.2}O_{1.9}$ could be indexed on a cubic fluorite-type lattice constant of 5.398(1) Å, 5.398(1) Å, 5.393(1) Å and 5.421(2) Å, respectively. Fig. 2 shows the idealized crystal structure of the conversion of a perovskite and perovskite-related structure materials into corresponding metal-doped fluorite-type structure. We have also performed energy dispersive X-ray spectroscopy (EDX) for the synthesized powder materials on the large surface area to confirm that the investigated samples were indeed the doped CeO_2 materials. The EDX data were found support the proposed chemical composition and is consistent with our earlier work [14,33].

In order to validate our proposed structural transformation reactions, we have performed HRTEM and ED studies on four different fluorite-type compounds such as $Ce_{0.9}In_{0.1}O_{1.95}$, $Ce_{0.8}In_{0.2}O_{1.9}$, $Ce_{0.9}Y_{0.1}O_{1.95}$, and $Ce_{0.8}Y_{0.2}O_{1.9}$ prepared by CO_2 mediated reactions. In Figs. 3 and 4, we show typical HRTEM images of 10 mol% and 20 mol% In_2O_3-doped CeO_2 synthesized from the corresponding In-doped $BaCeO_3$ at elevated temperature under CO_2, respectively. Shown in Figs. 5 and 6 are the corresponding data for the 10 mol% and 20 mol% Y_2O_3-doped CeO_2 synthesized from the layered structure Sr_2CeO_4.

As anticipated, the selected area ED patterns showed the lines only due to fluorite-type structure. We have successfully assigned all the diffraction lines into CeO_2 structure and are

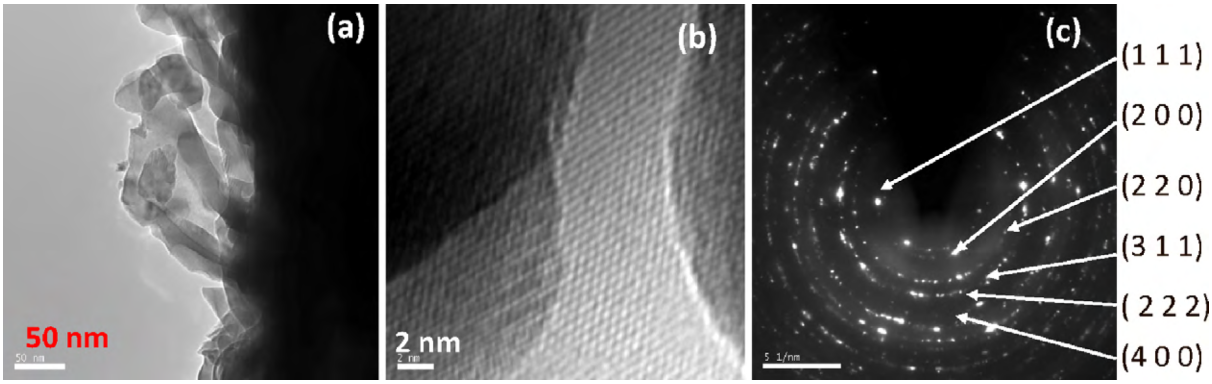

Fig. 5. TEM and HRTEM images of as-prepared (CO_2 capture method) powdered $Ce_{0.9}Y_{0.1}O_{1.95}$ from the corresponding 10 mol% Y-doped Sr_2CeO_4: (a) 100 nm scale, (b) 2 nm scale and (c) selected area electron diffraction pattern.

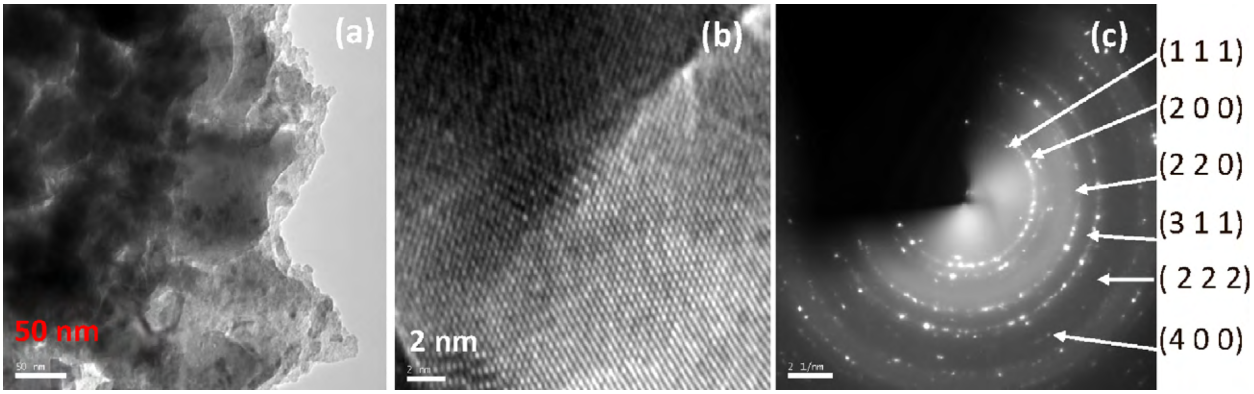

Fig. 6. TEM and HRTEM images of as-prepared (CO_2 capture method) powdered $Ce_{0.8}Y_{0.2}O_{1.9}$ from the corresponding 20 mol% Y-doped Sr_2CeO_4: (a) 100 nm scale, (b) 2 nm scale and (c) selected area electron diffraction pattern.

consistent with powder XRD data. We did not observe any main diffraction lines due to cubic In_2O_3 (e.g., 2 2 2 plane; $d \approx 2.92$ Å) joint committee on powder diffraction standard (JCPDS Card 060-416; JCPDS card no. 65-3170), hexagonal In_2O_3 (JCPDS card no. 22-0336), and Y_2O_3 (JCPDS card no. 25–1200) as well as the starting materials in the product, confirming the proposed transformation reaction. HRTEM shows the formation of nano-sized material which was found to consistent with several authors report of nano-sized CeO_2 [34–36]. The Y-sample was found have slightly larger particle size than that of the In-doped samples. Mechanistically, at elevated temperatures, the perovskite-like $BaCe_{1-x}In_xO_{3-\delta}$ ($x = 0.1$; 0.2) and layered perovskite-related $Sr_2Ce_{1-x}Y_xO_{4-\delta}$ ($x = 0.1$; 0.2) structures transform into their corresponding fluorite-type $Ce_{1-x}In_xO_{2-\delta}$ and $Ce_{1-x}Y_xO_{2-\delta}$ and $BaCO_3$. These fluorite-type phases of In-doped CeO_2 are stable up to ~800 °C [12,15].

4. Conclusions

In summary, the ED and TEM investigations strongly support the formation of In and Y-doped fluorite-type $Ce_{1-x}In_xO_{2-\delta}$ and $Ce_{1-x}Y_xO_{2-\delta}$ from three-dimensional (3D) perovskite-like $BaCe_{1-x}In_xO_{3-\delta}$ ($x = 0.1$; 0.2) and layered (two-dimensional) perovskite-related $Sr_2Ce_{1-x}Y_xO_{4-\delta}$ ($x = 0.1$; 0.2), respectively, under CO_2 mediated reaction at elevated temperature. The absence of any ED pattern that would correspond to the perovskite-like precursors and potential reaction by-products such as In_2O_3 and Y_2O_3 after the CO_2 reaction, evidently confirms the formation of a single-phase fluorite-type structure, which is consistent with ex situ and in situ powder X-ray diffraction (PXRD) analysis. The HRTEM images also confirmed expected nano-sized materials.

Acknowledgements

V. Thangadurai would like to thank the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Canada Foundation for Innovation (CFI) for the financial support.

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